

514,424

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

16 NOV 2004

(43) International Publication Date
4 December 2003 (04.12.2003)

PCT

(10) International Publication Number
WO 03/100801 A1(51) International Patent Classification⁷: H01G 9/20,
B41M 5/00

(74) Agent: DOKTER, Hendrik, Daniël; Octrooibureau Dokter, P.O. Box 657, NL-7300 AR Apeldoorn (NL).

(21) International Application Number: PCT/NL03/00357

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 15 May 2003 (15.05.2003)

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(25) Filing Language: Dutch

(26) Publication Language: English

(30) Priority Data:
1020701 29 May 2002 (29.05.2002) NL

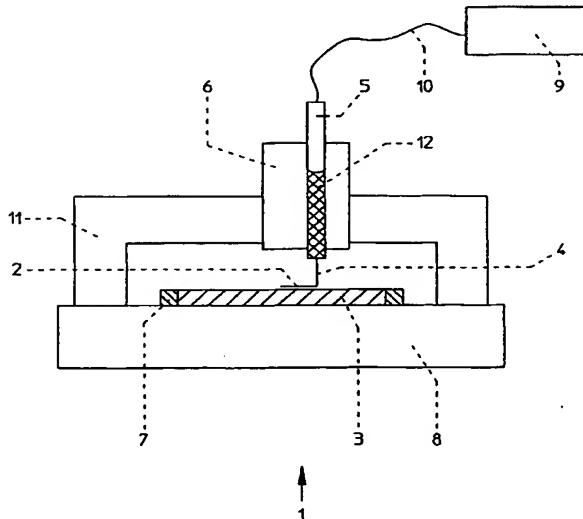
(71) Applicant (for all designated States except US): STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND [NL/NL]; Postbus 1, NL-1755 ZG Petten (NL).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD AND APPARATUS FOR APPLYING A LAYER OF A SECOND MATERIAL TO A LAYER OF A NANOCRYSTALLINE FIRST MATERIAL



WO 03/100801 A1

(57) Abstract: Method for applying a layer of a second material to a layer of a nonocrystalline first material, comprising the steps of (i) providing a layer of a nonocrystalline first material on a horizontal substrate, (ii) providing a liquid containing the second material, (iii) providing a tubular dispensing means to be disposed horizontally and provided with lateral outlet openings, (iv) disposing the dispensing means above the layer of nonocrystalline material, and (v) displacing the dispensing means and the layer of nanocrystalline material relative to each other in lateral horizontal direction of the dispensing means, while simultaneously supplying the liquid with the second material to the dispensing means, and apparatus for performing this method.

METHOD AND APPARATUS FOR APPLYING A LAYER OF A SECOND MATERIAL TO A LAYER OF A NANOCRYSTALLINE FIRST MATERIAL

The invention relates to a method for applying a layer of a second material to a layer of a nanocrystalline first material.

Such a method is known from European patent application 5 EP-A-1107333 for a photoelectric conversion device, where the manufacture of a work electrode for a photovoltaic element is described.

The work electrode described in this patent application comprises a conductive layer which is applied to a glass 10 substrate and to which are successively applied a first layer of a nanocrystalline titanium dioxide, provided with a dye sensitizer and a second layer of a thiocyanate acting as a charge transfer medium. The second layer is applied in known manner by using an Eppendorf to drip a determined amount of a 15 solution of the thiocyanate in acetonitrile onto the substrate with the first layer, wherein the substrate rests on a heating plate in order to evaporate the solvent.

The known method has the drawback that it is particularly difficult to apply a second layer that is homogenous onto a 20 first layer of a nanocrystalline material in reproducible manner. The thickness of the charge transfer layers described in the cited patent application amounted to between 15 µm and 30 µm.

Another drawback is the long period of time involved in 25 applying a layer of a sufficient width for a photovoltaic element.

A further drawback of the known method is that it is difficult to scale up, i.e. it cannot be readily applied for the manufacture of photovoltaic elements on industrial scale.

30 It is an object of the invention to provide a method in accordance with which it is possible in reproducible manner to apply a second layer that is homogenous onto a first layer of a nanocrystalline material.

It is a further object to provide a method in accordance with which a layer of a sufficient width for a photovoltaic element can be applied in a short period of time.

It is yet another object to provide a method which can be 5 readily applied for the manufacture of photovoltaic elements on industrial scale.

These goals are achieved with a method of the type stated in the preamble, which according to the invention comprises the steps of (i) providing a layer of a nanocrystalline first 10 material on a horizontal substrate, (ii) providing a liquid containing the second material, (iii) providing a tubular dispensing means to be disposed horizontally and provided with lateral outlet openings, (iv) disposing the dispensing means above the layer of nanocrystalline material, and (v) 15 displacing the dispensing means and the layer of nanocrystalline material relative to each other in lateral horizontal direction of the dispensing means, while simultaneously supplying the liquid with the second material to the dispensing means.

20 During performing of the fifth step (v) liquid flows from the dispensing means onto the layer of the nanocrystalline material, where the liquid firstly penetrates into the pores of this material and subsequently forms a layer on the material.

25 The liquid containing the second material to be provided in the second step (ii) is preferably a solution with this second material, from which the second material can be precipitated by evaporation of the solvent, but can also be the second material in liquid phase which solidifies after 30 being applied to the layer of nanocrystalline material.

The invention further relates to an apparatus for performing the above described method, which apparatus according to the invention comprises at least one tubular dispensing means to be disposed horizontally and provided 35 with lateral outlet openings, a liquid container and conduit means for carrying liquid from the liquid container to the at least one dispensing means.

One embodiment of an apparatus according to the invention is provided with displacing means for displacing the dispensing means and the layer of nanocrystalline material relative to each other in lateral horizontal direction of the 5 dispensing means, which displacing means comprise for instance a carrier displaceable in horizontal direction relative to the dispensing means for carrying and displacing a layer of nanocrystalline material in lateral direction relative to the dispensing means.

10 In an advantageous embodiment the displacing means comprise an XY table.

In an embodiment which is particularly suitable for use in applying a layer of a second material that is provided in dissolved state in a solvent, the apparatus according to the 15 invention is provided with heating means to heat a layer of a nanocrystalline material during performing of the method.

In one embodiment the tubular dispensing means is connected at a first outer end to a first liquid supply line and is closed at a second outer end. In this embodiment the 20 liquid to be dispensed is supplied via the first outer end of the tubular dispensing means and is deposited via the outlet openings onto the layer of nanocrystalline material.

In a subsequent embodiment the tubular dispensing means is connected at a first outer end to a first liquid supply 25 line, and is connected at a second outer end to a liquid circulation line or a second liquid supply line.

This latter embodiment is particularly suitable for use in applying a relatively wide layer. The tubular dispensing means herein forms part of a U-shaped structure, wherein the 30 dispensing means is suspended at a first outer end from a first liquid supply line, and at a second outer end is suspended from a liquid circulation line or from a second liquid supply line.

It has been found that an exceptionally homogenous layer 35 is applied with an apparatus according to the invention wherein the lateral outlet openings are provided in the top side of a horizontally disposed tubular dispensing means.

The tubular dispensing means preferably has a circular outer periphery in vertical cross-section.

A tubular dispensing means with a circular outer periphery has the advantage that the tube required for this purpose is commercially available in the desired sizes, so that the dispensing means can be manufactured in simple manner and at low cost.

The present invention will be elucidated hereinbelow on the basis of an embodiment of an apparatus and with reference 10 to the drawing.

Fig. 1 shows a front view of a simplified view of an embodiment of an apparatus 1 for applying a second layer of a soluble material to a first layer of a nanocrystalline material. The figure shows an L-shaped injection needle, a 15 part 2 of which is arranged horizontally above a horizontally placed copper substrate table 3, and a vertical part 4 of which is connected to a supply container 5 for a solution 12 of a material to be applied. The injection needle 2, 4 has an internal diameter of 0.4 mm. The horizontal part 2 thereof 20 forms the dispensing tube which is closed at its free outer end, and which is provided on its upper side with a number of outlet openings with a diameter of 0.1 mm (not shown). Supply container 5 and L-shaped injection needle 2, 4 are mounted on a height adjusting device 6 for adjusting the distance 25 between the dispensing tube 2 and a substrate with nanocrystalline layer laid on substrate table 3 (not shown). Substrate table 3 is displaceable in lateral horizontal direction of dispensing tube 2 (perpendicularly of the plane of the drawing) between longitudinal guides 7 over a heating 30 plate 8. The figure further shows another liquid metering pump 9 which is connected with a flexible conduit 10 to supply container 5 and a fixed yoke 11 for suspending the height adjusting device 6. Not shown is a switch box with measuring and control electronics for height adjusting device 35 6, the temperature adjustment of heating plate 8, the displacement of substrate table 3 and metering pump 9.

It is noted that the described embodiment serves to

elucidate the invention, and not to limit the scope of protection of the patent applied for. It is for instance possible to embody the tube part 2 as a horizontal part of a U-shaped injection needle. The width of the homogenous layer 5 laid on the layer of nanocrystalline material is after all determined by the length of the tube part 2, which length is inherently limited, at a determined number of outlet openings of a determined diameter, by the internal diameter of tube part 2. The use of a U-shaped injection needle achieves that 10 within these limitations this length is doubled, wherein liquid is fed via both outer ends to the horizontal part. It is further possible to increase the width of the homogenous layer by simultaneously displacing more than one tubular dispensing means above a substrate. It is also possible to 15 increase the width of the homogenous layer by replacing the substrate holder (the copper table 3), which is displaceable in longitudinal direction, with an XY table, i.e. a substrate holder displaceable in longitudinal direction and width. It is further possible to replace the copper table 3 which rests 20 on a heating plate 8 with a substrate holder provided with a heating element.

CLAIMS

1. Method for applying a layer of a second material to a layer of a nanocrystalline first material, comprising the steps of

(i) providing a layer of a nanocrystalline first material 5 on a horizontal substrate (3),

(ii) providing a liquid (12) containing the second material,

10 (iii) providing a tubular dispensing means (2) to be disposed horizontally and provided with lateral outlet openings,

(iv) disposing the dispensing means (2) above the layer of nanocrystalline material, and

15 (v) displacing the dispensing means (2) and the layer of nanocrystalline material relative to each other in lateral horizontal direction of the dispensing means (2), while simultaneously supplying the liquid (12) with the second material to the dispensing means (2).

2. Apparatus (1) for applying a layer of a second material to a layer of a nanocrystalline first material in accordance with a method as claimed in claim 1, comprising a tubular dispensing means (2) to be disposed horizontally and provided with lateral outlet openings, a liquid container (5) and conduit means (4, 9, 10) for carrying liquid (12) from the liquid container (5) to the dispensing means (2).

25 3. Apparatus (1) as claimed in claim 2, characterized in that it is provided with displacing means (3, 7) for displacing the dispensing means (2) and the layer of nanocrystalline material relative to each other in lateral horizontal direction of the dispensing means (2).

30 4. Apparatus (1) as claimed in claim 3, characterized in that the displacing means comprise a carrier (3) displaceable in horizontal direction relative to the dispensing means (2) for carrying and displacing a layer of nanocrystalline material in lateral direction relative to the dispensing

means (2).

5. Apparatus (1) as claimed in either of the claims 3-4,
characterized in that the displacing means comprise an XY
table.

5 6. Apparatus (1) as claimed in any of the claims 2-5,
characterized in that it is provided with heating means (8)
for heating a layer of a nanocrystalline material during
performing of the method.

7. Apparatus (1) as claimed in any of the claims 2-6,
10 **characterized in that** the tubular dispensing means (2) is
connected at a first outer end to a first liquid supply line
(4) and is closed at a second outer end.

8. Apparatus (1) as claimed in any of the claims 2-6,
characterized in that the tubular dispensing means is
15 connected at a first outer end to a first liquid supply line,
and is connected at a second outer end to a liquid
circulation line or a second liquid supply line.

9. Apparatus (1) as claimed in any of the claims 2-8,
characterized in that the lateral outlet openings are
20 provided in the top side of a horizontally disposed tubular
dispensing means (2).

10. Apparatus (1) as claimed in any of the claims 2-9,
characterized in that the tubular dispensing means (2) has a
circular outer periphery in vertical cross-section.

25 11. Apparatus (1) as claimed in any of the claims 2-10,
characterized in that the conduit means comprise a liquid
metering pump (9).

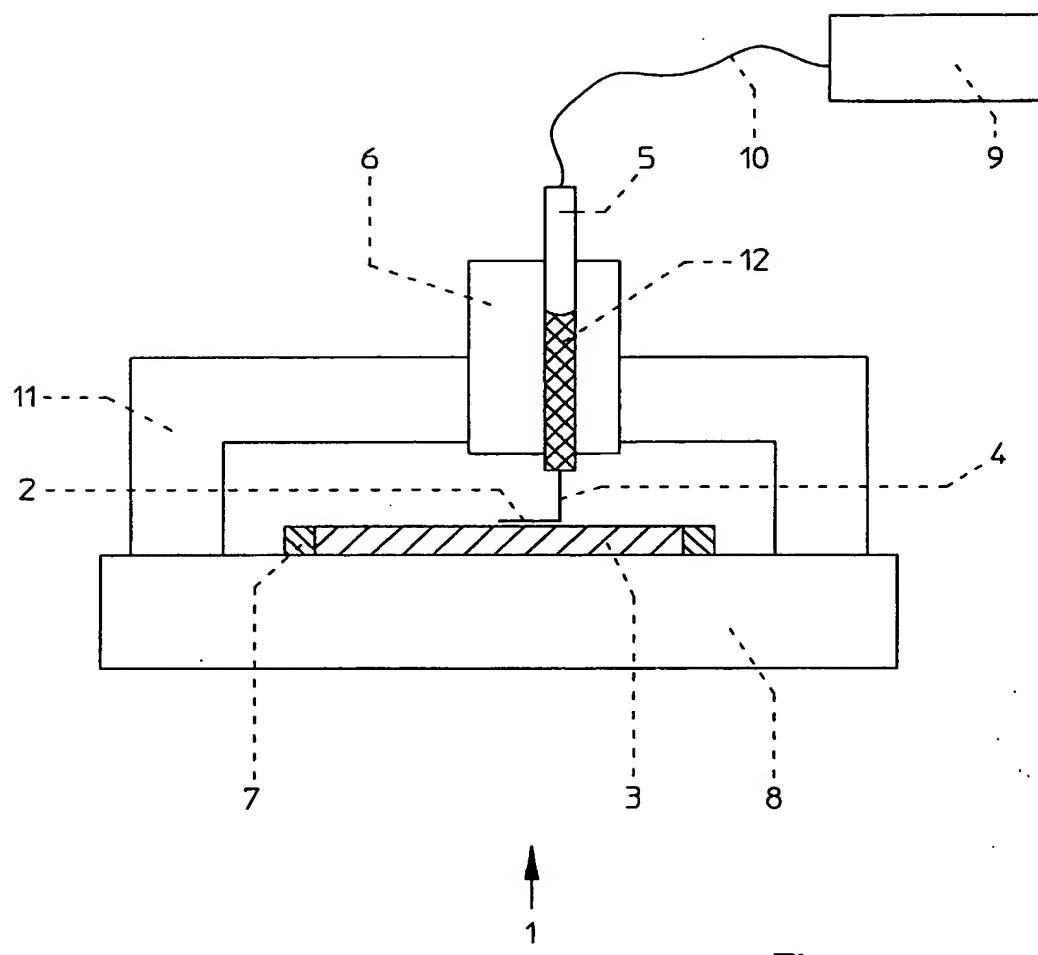


Fig. 1

INTERNATIONAL SEARCH REPORT

PCT/NL 03/00357

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 H01G9/20 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L H01G B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 930 641 A (SEIKO EPSON CORP) 21 July 1999 (1999-07-21) paragraphs '0006!, '0007!, '0015!, '0018!, '0021!, '0061!, '0062!, '0067!, '0068!, '0071!, '0072!, '0076!- '0078!; figures 1-5,18-20 ---	1-3,6,9
X	TENG K F ET AL: "METALLIZATION OF SOLAR CELLS WITH INK JET PRINTING AND SILVER METALLO-ORGANIC INKS" IEEE TRANSACTIONS ON COMPONENTS, HYBRIDS, AND MANUFACTURING TECHNOLOGY, IEEE INC. NEW YORK, US, VOL. 11, NO. 3, 1 September 1988 (1988-09-01), pages 291-297, XP000112927 ISSN: 0148-6411 the whole document ----	1-6

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the International search

16 July 2003

Date of mailing of the International search report

25/07/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Visentin, A

INTERNATIONAL SEARCH REPORT

PCT/NC 03/00357

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 093 167 A (SEMICONDUCTOR ENERGY LAB) 18 April 2001 (2001-04-18) paragraphs '0016!-'0022!, '0170!-'0173!; figures 1-4,16 ---	1-3,9,10
A	DANZEBRINK R ET AL: "Deposition of micropatterned coating using an ink-jet technique" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 351, no. 1-2, 30 August 1999 (1999-08-30), pages 115-118, XP004183077 ISSN: 0040-6090 the whole document ---	1-6,9,10
A	EP 1 107 333 A (FUJI PHOTO FILM CO LTD) 13 June 2001 (2001-06-13) cited in the application paragraphs '0041!, '0042! ---	1
A	EP 1 127 707 A (EASTMAN KODAK CO) 29 August 2001 (2001-08-29) page 2; claims 1-7 ---	1,2
A	HEBNER T R ET AL: "LOCAL TUNING OF ORGANIC LIGHT-EMMITTING DIODE COLOR BY DYE DROPLET APPLICATION" APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 73, no. 13, 28 September 1998 (1998-09-28), pages 1775-1777, XP000784155 ISSN: 0003-6951 the whole document ---	1,2
A	US 6 087 196 A (WU CHUNG CHIH ET AL) 11 July 2000 (2000-07-11) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/NL 03/00357

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
EP 0930641	A 21-07-1999	JP EP TW US	11204529 A 0930641 A2 383280 B 2003003231 A1	30-07-1999 21-07-1999 01-03-2000 02-01-2003
EP 1093167	A 18-04-2001	CN EP JP TW	1291786 A 1093167 A2 2001185354 A 480722 B	18-04-2001 18-04-2001 06-07-2001 21-03-2002
EP 1107333	A 13-06-2001	JP EP JP	2001230435 A 1107333 A2 2001230434 A	24-08-2001 13-06-2001 24-08-2001
EP 1127707	A 29-08-2001	EP JP US	1127707 A1 2001287438 A 2002086112 A1	29-08-2001 16-10-2001 04-07-2002
US 6087196	A 11-07-2000	AU EP JP WO	2481599 A 1051738 A2 2002502098 T 9939373 A2	16-08-1999 15-11-2000 22-01-2002 05-08-1999